

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) **EP 1 067 155 A1**

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
10.01.2001 Bulletin 2001/02

(51) Int. Cl.⁷: **C09B 5/14**, **C09D 11/00**,
B41M 5/00, **B41J 2/01**

(21) Application number: **99909295.0**

(86) International application number:
PCT/JP99/01436

(22) Date of filing: **23.03.1999**

(87) International publication number:
WO 99/48981 (30.09.1999 Gazette 1999/39)

(84) Designated Contracting States:
CH DE FR GB IT LI

(30) Priority: **25.03.1998 JP 9519998**
07.08.1998 JP 22477698

(71) Applicant:
Nippon Kayaku Kabushiki Kaisha
Tokyo 102-8172 (JP)

(72) Inventors:
• **MATSUMOTO, Hiroyuki**
Omiya-shi Saitama-ken 331-0044 (JP)

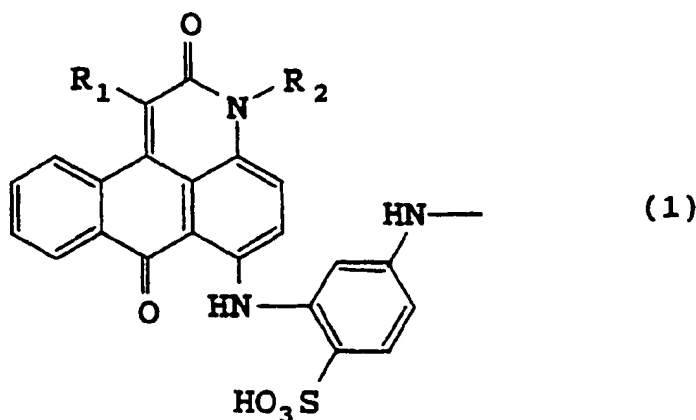
• **MURAKAMI, Yasuo**
Kawaguchi-shi Saitama-ken 332-0032 (JP)
• **SHIRASAKI, Yasuo**
Omiya-shi Saitama-ken 330-0826 (JP)
• **FUJII, Katsunori**
Kawaguchi-shi Saitama-ken 334-0075 (JP)
• **TABEL, Toru**
Kitamoto-shi Saitama-ken 364-0007 (JP)

(74) Representative:
Gille Hrabal Struck Neidlein Prop Roos
Patentanwälte
Brucknerstrasse 20
40593 Düsseldorf (DE)

(54) **NOVEL ANTHRAPHYRIDONE COMPOUNDS, WATER-BASED MAGENTA INK COMPOSITION, AND METHOD OF INK-JET RECORDING**

(57) The present invention provides novel anthrapyridone compounds or salts thereof which have a magenta hue and vividness suitable for ink-jet recording and give the recorded material having a high fastness in light fastness and water fastness.

That is, the present invention relates to an anthrapyridone compound represented by Formula A-B or the salt thereof, wherein A is the dyestuff residue represented by Formula (1)



(in the formula, R₁ is hydrogen atom or an alkoxy carbonyl group and R₂ is hydrogen atom or methyl group); and

EP 1 067 155 A1

EP 1 067 155 A1

B is hydrogen atom or a substituent group on the dyestuff residue A, a water-based magenta ink composition which includes the said compound and an ink-jet recording method which uses the said compound.

Description**TECHNICAL FIELD**

- 5 **[0001]** The present invention relates to a novel anthrapyridone compound, a water-based magenta ink composition, and a method of ink-jet recording.

BACKGROUND ART

- 10 **[0002]** Diverse ink jetting processes have been developed for the recording method by means of ink-jet printer, and any process comprises generating ink droplets to deposit them onto various recording materials (such as paper, film, cloth) for recording. The recording method by means of ink-jet printer has rapidly been spread in recent years and will be propagated in future because the method brings about no noise due to the system in which a recording head does not contact with the recording material and because the method advantageously allows the printer to become down-sized easily, to work in a high-speed and to give color printing. For recording an image information or a character information pictured on a computer color display in color by means of an ink-jet printer, the information is generally printed according to subtractive color mixing of inks of four colors, namely yellow(Y), magenta(M), cyan(C) and black(K). In order to print reproducibly an image pictured by additive color mixing of R, G, B on a CRT display as faithfully as possible according to subtractive color mixing, the dyestuffs used, especially ones for a YMC ink, are desired to have color hues close to the respective standards of YMC("Japan Color Standard Paper" published by Japan Printing Machinery Manufacturers Association) and vividness. Additionally, it is required that the resulting ink composition is stable for long-term storage and that the resulting printed image is of a high optical density and has excellent fastness including water fastness and light fastness. The present invention relates to a magenta ink.

- 25 **[0003]** Ink-jet printers are increasingly used in a wide range from a small one for OA to a big one for industrial use. So, excellence in fastness such as water fastness and light fastness of the printed image is more strictly demanded. The water fastness is substantially improved by coating inorganic micro particles such as porous silica, which can absorb dyestuff from ink, on a paper sheet with PVA resin. Various coated sheets for ink-jet printing are already available on the market. But light fastness is not yet improved by an established technique. Of tetrachromatic colors of YMCK, magenta especially has many dyestuffs which are naturally weak in light fastness, and the improvement is an important problem to be solved.

- 30 **[0004]** The chemical skeletal structure of magenta dyestuffs used in a water-soluble ink for ink-jet recording is represented by a xanthene type disclosed by JP Laid-Open No.89811/1979, JP Laid-Open No.60053/1996 and JP Laid-Open No.143798/1996, or an azo type using the H acid disclosed by JP Laid-Open No.62562/1986, JP Laid-Open No.156168/1987, JP Laid-open No.203970/1991, JP Laid-Open No.157698/1995 and JP Publication No.78190/1995.
- 35 The xanthene type is indeed excellent in hue and vividness, but is inferior in light fastness. The azo type using the H acid is good in hue and water fastness, but is inferior in light fastness and vividness. As disclosed by JP Laid-Open No.203970/1991, for example, some magenta dyestuffs being excellent in vividness and light fastness have been developed, but are still inferior in light fastness to the other hue dyestuffs such as yellow dyestuffs and cyan dyestuffs represented by copper phthalocyanine type.

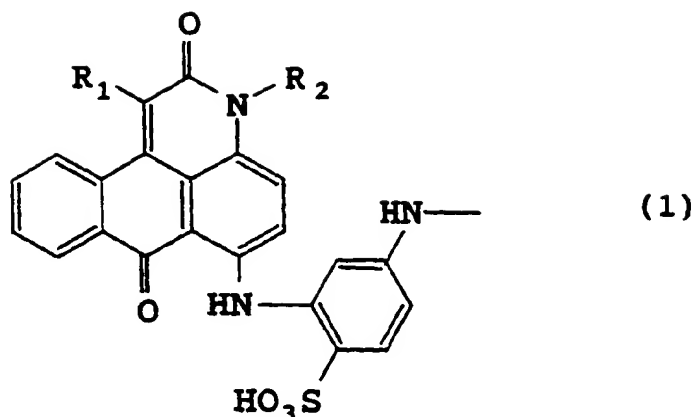
- 40 **[0005]** Alternatively, for a chemical skeletal structure of magenta dyes excellent in vividness and light fastness, an anthrapyridone type is known as disclosed by JP Laid-Open No.74173/1984 and JP Laid-Open No.16171/1990, but can not yet show any satisfactory properties in hue, vividness, light fastness, water fastness and stability in solution.

- 45 **[0006]** A object of the present invention is to provide a water-based magenta ink composition which has a wide range of blend color in hue and vividness suitable for ink-jet recording and supplies the recorded material with a high fastness in light fastness and water fastness.

DISCLOSURE OF THE INVENTION

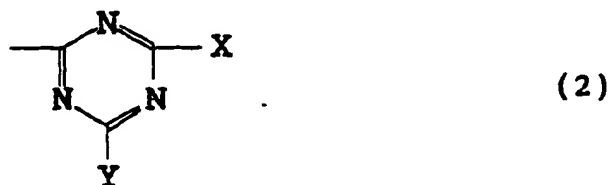
- 50 **[0007]** The present inventors made a diligent study to solve the above problem and, as a result, have completed the present invention. Namely, the present invention is as follows:

(1) An anthrapyridone compound represented by Formula A-B or the salt thereof, wherein A is the dyestuff residue represented by Formula (1)



20 (In the formula, R₁ is hydrogen atom, an alkoxycarbonyl group or a benzoyl group and R₂ is hydrogen atom or methyl group); and B is hydrogen atom or a substituent group on the dyestuff residue A.

(2) An anthrapyridone compound or the salt thereof according to term (1), wherein said B is an acyl group or a group represented by Formula (2)



35 (In the formula, each X and Y is independently chlorine atom, hydroxyl group, amino group, monoethanolamino group, diethanolamino group, morpholino group or anilino group(which may have one or more substituent selected from the group consisting of sulfonate group, carboxyl group, methyl group and chlorine atom)).

(3) An anthrapyridone compound or the salt thereof according to term (2), wherein said X is anilino group(which may have one or more substituent selected from the group consisting of sulfonate group and carboxyl group), and Y is chlorine atom, hydroxyl group, amino group, monoethanolamino group, diethanolamino group or morpholino group.

(4) An anthrapyridone compound or the salt thereof according to term (2), wherein said acyl group is benzene sulfonyl group, tosyl group, 2-carboxy-benzoyl group or 3,4-dicarboxy-benzoyl group.

(5) An anthrapyridone compound or the salt thereof according to term (1), wherein said R₁ is hydrogen atom; R₂ is methyl group.

(6) A water-based magenta ink composition which comprises containing the anthrapyridone compound or the salt thereof according to any one of term (1) to (5).

(7) A water-based magenta ink composition according to term (6), wherein said composition contains water and an organic solvent.

(8) A water-based magenta ink composition according to term (6) or (7), wherein the content of inorganic salt included in said anthrapyridone compound or the salt is 1% by weight or less.

(9) A water-based magenta ink composition according to any one of term (6) to (8), wherein said composition is prepared for ink-jet recording.

(10) A method for ink-jet recording which comprises using the water-based magenta ink composition according to any one of term (6) or (8) as an ink, in the recording way that ink droplets are ejected responding to record signals to record onto a recording material.

(11) A method for ink-jet recording which comprises using both the water-based magenta ink composition according to any one of term (6) or (8) as an magenta ink and a water-based ink containing water-soluble metal phthalate-

cyanine dyestuff as a cyan ink, in the recording way that ink droplets are ejected responding to record signals to record onto a recording material.

(12) A method for ink-jet recording according to term (11), wherein said recording material is an information transmission sheet.

5 (13) A method for ink-jet recording according to term (12), wherein said information transmission sheet is a surface-treated sheet.

(14) An ink-jet printer which comprises being equipped with both a container receiving the water-based magenta ink composition according to any one of term (6) or (8) and a container receiving the water-based cyan ink composition containing water-soluble metal phthalocyanine dyestuff.

10 (15) An anthrapyridone compound or the salt according to term (1), wherein R_1 is hydrogen atom or a lower alkoxycarbonyl group; R_2 is methyl group; and B is hydrogen atom or a C1-C4 alkoxycarbonyl group.

BRIEF DESCRIPTION OF THE DRAWINGS

15 [0008]

Fig.1 depicts an example of chromaticity diagram expressing the color ranges by the compound of the present invention as well as the dye of a Reference.

20 Description of Symbols

[0009] In Fig.1, the axis X represents a^* and the axis Y represents b^* on the $L^* a^* b^*$ colorimetric system. Y shows yellow, R shows red, M shows magenta, B shows blue, C shows cyan and G shows green. The solid line expresses the range of blend color by the compound of Example 2 and the dotted line expresses the range of blend color by the standard in "Japan Color Standard Paper". The plot G in the solid line shows blend color(Reference value) obtained by printing C.I.Direct Yellow 86 and C.I.Direct Blue 199 overlapped.

BEST MODE FOR CARRYING OUT THE INVENTION

30 [0010] The novel anthrapyridone compound of the present invention is represented by Formula A-B. A is the dyestuff residue represented by Formula (1), and B is hydrogen atom or a substituent group on the dyestuff residue A. Namely, the present invention is an anthrapyridone compound characterized by having the group represented by Formula (1) as the dyestuff residue. The anthrapyridone compound, which has the group represented by Formula (1) as the dyestuff residue, is preferably a water-soluble compound used for a magenta (bluish red) dyestuff component.

35 [0011] The alkoxycarbonyl group in R_1 includes a C1-C4 alkoxycarbonyl group such as methoxycarbonyl group, ethoxycarbonyl group, n-propoxycarbonyl group, isopropoxycarbonyl group, and n-butoxycarbonyl group.

[0012] The substituent group represented by B on the dyestuff residue A is not particularly limited provided that it is able to substitute on a nitrogen atom. It includes an acyl group, a substituent represented by Formula (2) and a C1-C4 alkyl group which may have substituents.

40 [0013] The preferable example of the dyestuff residue A can be presented when R_1 is hydrogen atom and R_2 is methyl group in Formula (1).

[0014] The acyl group includes a substituted or unsubstituted benzenesulfonyl group, a substituted or unsubstituted alkylsulfonyl group, a substituted or unsubstituted benzoyl group, and a substituted or unsubstituted alkoxycarbonyl group. The substituent group on the benzene nucleus in these above groups includes a lower(C1-C4)alkyl group, phenyl group, a halogen atom, nitro group, amino group, hydroxy group, and carboxyl group; and may additionally have a substituent group as shown above if possible. A substituent group on the alkyl group includes the substituent group on the benzene nucleus as shown above other than the alkyl group. The acyl group includes benzenesulfonyl group; a lower alkyl-substituted benzenesulfonyl group such as tosyl; a halogenobenzenesulfonyl group such as 4-chlorobenzenesulfonyl group and 4-bromobenzenesulfonyl group; a (C1-C4)alkylsulfonyl group such as methylsulfonyl group and ethylsulfonyl group; a optionally substituted benzoyl group such as benzoyl group and 3,4-dicarboxybenzoyl group; a lower alkylcarbonyl group such as phenylacetyl group and acetyl group; a (C1-C4)alkoxycarbonyl group such as methoxycarbonyl group, ethoxycarbonyl group, propoxycarbonyl group, butoxycarbonyl group and benzyloxycarbonyl group.

50 [0015] The anilino group, which may have one or more substituents selected from the group consisting of sulfonate group, carboxyl group, methyl group and chlorine atom, includes 2,5-disulfoanilino group, 3-sulfoanilino group, 2-sulfoanilino group, 4-sulfoanilino group, 2-carboxy-4-sulfoanilino group and 2-carboxy-5-sulfoanilino group.

[0016] X in Formula (2) is preferably an anilino group which may have one or more substituents, more preferably an anilino group having at least one sulfonate group.

[0017] The preferable Y is amino group or hydroxy group.

[0018] The preferable anthrapyridone compound represented by Formula A-B of the present invention can be presented when R₁ is hydrogen atom or a lower alkoxy carbonyl group, more preferably hydrogen atom; and R₂ is methyl group in Formula (1); and B is represented by Formula (2) wherein X is an amino group having at least one sulfonyl group and Y is hydroxy group or amino group.

5 **[0019]** The anthrapyridone compound and the salt thereof, in which R₁ is hydrogen atom or a lower alkoxy carbonyl group; R₂ is methyl group; and B is hydrogen atom or a lower (C1-C4) alkoxy carbonyl group, is important as an intermediate for synthesizing the other anthrapyridone compounds of the present invention.

[0020] The typical examples of the anthrapyridone compound represented by Formula A-B of the present invention are shown in Table 1. In Table 1, (S) means sulfonate group, 2(S) means disulfonate group, (K) means carboxy group, 10 2(K) means dicarboxy group, E means ethoxycarbonyl group, M means methoxycarbonyl group, Ph means phenyl group and Bz means benzoyl group.

15

20

25

30

35

40

45

50

55

Table 1

5	No.	A		B		
		Formula (1)			Formula (2)	
10		R ₁	R ₂		X	Y
	1	H	CH ₃	COCH ₃		
	2	H	CH ₃	H		
15						
	3	H	CH ₃		2,5-2(S)-anilino	Cl
	4	H	CH ₃		2,5-2(S)-anilino	OH
20						
	5	H	CH ₃		2,5-2(S)-anilino	NH ₂
	6	H	CH ₃		2,5-2(S)-anilino	morpholino
25						
	7	H	CH ₃		2,5-2(S)-anilino	di(hydroxyethyl)amino
	8	H	CH ₃		2,5-2(S)-anilino	hydroxyethylamino
30						
	9	H	CH ₃		3-(S)-anilino	Cl
	10	H	CH ₃		3-(S)-anilino	OH
	11	H	CH ₃		2-(S)-anilino	Cl
35						
	12	H	CH ₃		2-(S)-anilino	OH
	13	H	CH ₃		4-(S)-anilino	Cl
40						
	14	H	CH ₃		4-(S)-anilino	OH
	15	H	CH ₃		2-(K)-4-(S)-anilino	Cl
45						
	16	H	CH ₃		2-(K)-4-(S)-anilino	OH
	17	H	CH ₃		2-(K)-4-(S)-anilino	NH ₂

	18	H	CH ₃	2-(K)-5-(S)-anilino	Cl
5	19	H	CH ₃	2-(K)-5-(S)-anilino	OH
	20	H	CH ₃	2-(K)-5-(S)-anilino	NH ₂
10	21	E	CH ₃	2,5-2(S)-anilino	Cl
	22	E	CH ₃	2,5-2(S)-anilino	OH
	23	M	H	2,5-2(S)-anilino	Cl
15	24	M	H	2,5-2(S)-anilino	OH
	25	H	CH ₃	2,5-2(S)-anilino	2,5-2(S)-anilino
20	26	H	CH ₃	2,5-2(S)-anilino	2-(S)-anilino
	27	H	CH ₃	CH ₃ PhSO ₂	
	28	H	CH ₃	PhSO ₂	
25	29	H	CH ₃	Bz	
	30	H	CH ₃	3,4-2(K)-Bz	
30	31	H	CH ₃	CH ₃ PhSO ₂	
	32	H	CH ₃	4-Cl-PhSO ₂	
	33	H	CH ₃	Ph-CH ₂ CO	
35	34	H	CH ₃	C ₂ H ₅ OCO	
	35	H	CH ₃	Ph-CH ₂ OCO	
40	36	E	CH ₃	CH ₃ PhSO ₂	
	37	E	CH ₃	PhSO ₂	
	38	E	CH ₃	Bz	
45	39	E	CH ₃	3,4-2(K)-Bz	
	40	E	CH ₃	CH ₃ PhSO ₂	
50	41	E	CH ₃	4-Cl-PhSO ₂	
	42	E	CH ₃	PhCH ₂ CO	

55

	4 3	E	CH ₃	C ₂ H ₅ OCO	
5	4 4	E	CH ₃	PhCH ₂ OCO	
	4 5	E	CH ₃	CH ₃ CO	
10	4 6	E	CH ₃	H	
	4 7	Bz	CH ₃	2,5-2(S)-anilino	OH
15	4 8	E	CH ₃	2(K)-Bz	

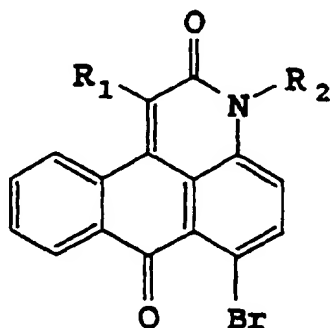
20 [0021] The anthrapyridone compound of the present invention can be produced, for example, by a following procedure.

[0022] Namely, the anthrapyridone bromo-compound represented by Formula (3)

25

30

35



(3)

(in the formula, R₁ and R₂ are same as described before) can be condensed with 5-acetylamino-2-sulfoaniline by the Ullmann reaction to obtain the above No.1 compound. The acetyl group of the obtained compound is then removed by hydrolysis to obtain the above No.2 compound that appears when B is hydrogen atom.

[0023] In order to obtain a compound in which B is the substituent represented by Formula (2) and X is the other group than chlorine atom and hydroxyl group the compound responding to said other group, for example, an amine compound such as aniline, is condensed with 2,4,6-trichloro-s-triazine (cyanuric chloride) to give the responding first condensate, which is then condensed with the No.2 compound to give the second condensate wherein X is for example the responding amino group and Y is chlorine atom. The second condensate is hydrolyzed to obtain the compound wherein Y is hydroxyl group. Furthermore, in order to obtain a compound in which Y is the other group than chlorine atom and hydroxyl group, the above second condensate wherein Y is chlorine atom is condensed with a responding amine compound for the third condensation.

[0024] In order to obtain a compound in which B is the other group than the substituent represented by Formula (2), the No.2 compound is satisfactorily reacted with an acylating agent. The acylating agent, which is for example an acyl chloride responding to the above acyl group, includes a substituted or unsubstituted benzenesulfonyl chloride, a substituted or unsubstituted alkylsulfonyl chloride, a substituted or unsubstituted benzoyl chloride, and a substituted or unsubstituted alkoxy carbonyl chloride; to be concrete, benzenesulfonyl chloride, toluenesulfonyl chloride, 4-chlorobenzenesulfonyl chloride, 4-bromobenzenesulfonyl chloride, methylsulfonyl chloride, ethylsulfonyl chloride, benzoyl chloride, 3,4-dicarboxybenzoyl chloride, phenylacetic acid chloride, acetic acid chloride, methoxycarbonyl chloride, ethoxycarbonyl chloride, prooxycarbonyl chloride, butoxycarbonyl chloride and benzyloxycarbonyl chloride.

[0025] The compound thus obtained exists as a free acid or the salt thereof. The alkali metal salt, the alkali earth

metal salt, the alkylamine salt, the alkanolamine salt or the ammonium salt may be used in the present invention. The preferable salt includes an alkali metal salt such as the sodium salt, the potassium salt and the lithium salt; an alkanolamine salt such as the monoethanolamine salt, the diethanolamine salt, the triethanolamine salt, the monoisopropanolamine salt, the diisopropanolamine salt and the triisopropanolamine salt; and the ammonium salt.

5 [0026] The water-based magenta ink composition of the present invention can be obtained by dissolving the compound represented by Formula A-B or the salt thereof in water or a hydrous solvent (an organic solvent containing water will be described later). The preferable ink pH is about 6 to 11. For use in an ink-jet recording printer, it is preferable to use a water-based ink composition whose dyestuff component contains an amount as little as possible of an inorganic material such as the chloride and the sulfate of a metal positive ion. For example, the total content of sodium chloride
10 and sodium sulfate in the dyestuff component is 1% by weight or less relative to the total amount of a compound represented by Formula A-B or the salt thereof.

[0027] In order to produce the dyestuff component (a compound represented by Formula A-B or the salt thereof) of the present invention having a low content of inorganic salt, it is sufficient to conduct a desalting treatment, for example, by a conventional method such as reverse osmotic membrane or by stirring a dry product or a wet cake of the anthrapyridone of the present invention in a mixed solvent of methanol and water, then filtering and drying. The alcohol content of the mixed solvent in the latter treatment is 30% by weight to 95% by weight, preferably 40% by weight to 85% by weight relative to the total mixed solvent. The amount of the mixed solvent is not limited, but is generally 1 to 200 times by volume, preferably 2 to 100 times by volume that of the wet cake.

[0028] The content of NaCl and N_2SO_4 in inorganic salts can be determined, for example, through measuring Cl^- and SO_4^{2-} respectively according to ion chromatography. Heavy metals can be determined according to atomic absorption spectrometry or Inductively Coupled Plasma(ICP) emission spectrometry; Ca^{2+} and Mg^{2+} can be determined according to ion chromatography, atomic absorption spectrometry or CIP emission spectrometry.

[0029] The water-based ink composition of the present invention is prepared by using water as a medium, containing the anthrapyridone compound or the salt thereof preferably by 0.1 to 20% by weight, more preferably by 1 to 10% by weight, more preferably 2 to 8% by weight. The water-based ink composition of the present invention also may contain a water-soluble organic solvent by 60% by weight or less, preferably 50% by weight, more preferably 40% or less, especially preferably 30% or less. The lower limit may be 0% by weight, but is generally 5% or more, more preferably 10% by weight or more, most preferably 10 to 30% by weight. The water-based ink composition of the present invention may contain ink regulators by 0 to 10% by weight, preferably 5% by weight or less. The remainder except the above
25 components is water.

[0030] The usable water-soluble organic solvent includes a C1 - C4 alkanol such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, secondary butanol and tertiary butanol; a carboxylic amide such as N,N-dimethylformamide and N,N-dimethylacetamide; a lactam such as ϵ -caprolactam and N-methylpyrrolidin-2-one; urea; a cyclic urea such as 1,3-dimethylimidazolidin-2-one or 1,3-dimethylhexahydropyrimidin-2-one; a ketone or a keto-alcohol such as acetone, methyl ethyl ketone, and 2-methyl-2-hydroxypentan-4-one; an ether such as tetrahydrofuran and dioxane; mono-, oligo- or poly-alkylene glycol or thioglycol having C2 - C6 alkylene units, such as ethylene glycol, 1,2- or 1,3-propylene glycol, 1,2- or 1,4-butyleneglycol, 1,6-hexylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, thiodiglycol, polyethylene glycol and polypropylene glycol; polyols (triols) such as glycerin and hexane-1,2,6-triol; C1 - C4 alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monomethyl ether, and triethylene glycol monoethyl ether; γ -butyrolactone; and dimethylsulfoxide. These solvents may be used in a combination of the two or more.

[0031] The effective examples of water-miscible organic solvents are N-methylpyrrolidin-2-one and mono-, di- or tri-alkylene glycol having C2 - C6 alkylene units, preferably mono-, di- or triethylene glycol, dipropylene glycol, glycerine, and dimethylsulfoxide. N-methylpyrrolidin-2-one, ethylene glycol, diethylene glycol, N-methyl-2-pyrrolidone, glycerine, and dimethylsulfoxide are especially preferably used.

[0032] The ink regulators, which are all the components except water, a dyestuff component and a water-soluble organic solvent, include a preservative, a pH adjusting agent, a chelating agent, a rust preventive, a water-soluble ultra-violet absorbing agent, a water-soluble polymeric compound, a dyestuff dissolving agent, and a surfactant. The preservative includes sodium dehydroacetate, sodium sorbate, sodium 2-pyridinethiol-1-oxide, sodium benzoate and sodium pentachlorophenol. The pH adjusting agent includes any substance that can control the ink pH within a range of 6 to 11 with no adverse effect on the ink preparation. The examples are alkanolamines such as diethanolamine and triethanolamine; alkali metal hydroxides such as lithium hydroxide, sodium hydroxide, and potassium hydroxide; ammonium hydroxide; or alkali metal carbonates such as lithium carbonate, sodium carbonate and potassium carbonate. The chelating reagent includes sodium ethylenediaminetetraacetate, sodium nitrilotriacetate, sodium hydroxyethylenediaminetriacetate, sodium diethylenetriaminepentaacetate, and sodium uramil diacetate. The rust preventive includes acidic hyposulfite salts, sodium thiosulfate, ammonium thioglycolate, diisopropylammonium nitrite, tetranitrate pentaerythritol, and dicyclohexylammonium nitrite.

[0033] The ink composition of the present invention is prepared by adding the above dyestuff and the above water-soluble organic solvent and the ink regulators as necessary into water such as distilled water containing no impurities and mixing them together. Alternatively, the dyestuff may be added in a mixture of water, the above water-soluble organic solvent and the ink regulators to dissolve. The resulting ink composition may be filtered, if necessary, to remove the contaminants from the composition.

[0034] A recording material used in ink-jet recording includes an information transmission sheet such as paper and film, fiber and leather. The information transmission sheet is defined to be a printing sheet that requires no special pre-treatment for printing and no post-treatment after printing by an ink-jet printer.

[0035] It is preferable that the information transmission sheet is surface-treated and, practically, is coated with an ink-acceptable layer on the basement material. The ink-acceptable layer can be supplied, for example, by impregnating or coating a cationic polymer on the above basement material; or by coating an inorganic fine-grain being enable of absorbing the dyestuff from an ink such as porous silica, alumina sol and special ceramic together with a hydrophilic polymer such as polyvinyl alcohol and polyvinyl pyrrolidone on the above basement material. The sheet supplied with the ink-acceptable layer is generally called an ink-jet special paper (film) or a glossy paper (film), and is available on the market, for example, as Pictorico (by Asahi Glass KK), Color BJ Paper, Color BJ Photofilm sheet (by Canon KK), Color Image Jet special paper (by Sharp KK), Superfine special glossy film (by Seiko Epson KK) and Pictafine (by Hitachi Maxell KK). The sheet can be of course used for a plain paper.

[0036] A method for ink-jet recording of the present invention can be carried out, for example, by setting an ink-jet printer with the container containing the above water-base magenta ink composition, and then recording conventionally on a recording material. The ink-jet printer includes a piezo type printer using mechanical vibration and a bubble-jet type printer using bubbles generated by heating.

[0037] In the method for ink-jet recording of the present invention, the above water-based magenta ink composition is generally used together with a yellow ink composition, a cyan ink composition, and a black ink composition as necessary. The cyan ink composition, if it contains a soluble metal phthalocyanine dyestuff, is used together with the above water-based magenta ink composition to give a favorable result that the color tone hardly changes in a light fastness test after color-mixing. Metals in the water-soluble metal phthalocyanine dyestuff includes copper, nickel and aluminum, and copper is preferable. The water-soluble copper phthalocyanine dyestuff includes C.I. direct blue 86, C.I. direct blue 87, C.I. direct blue 199, C.I. acid blue 249, C.I. reactive blue 7, C.I. reactive blue 15, C.I. reactive blue 21 and C.I. reactive blue 71.

[0038] The water-based cyan ink composition containing the water-soluble metal phthalocyanine dyestuff is produced, for example, by a method similar to that for the above water-based magenta ink composition, being injected in a container, which is set at the prescribed position of an ink-jet printer to use in the same way as another container containing the above water-based magenta ink composition is.

[0039] The water-based ink composition of the present invention can give an ideal magenta color which has vividness, color tone close to that indicated in the above "Japan Color Standard Paper published by Japan Printing Machinery Manufacturers Association", high tinge and moderate blueness, and therefore, can be used together with a yellow or cyan ink to give a wide visible range of color tone. Further, the composition, if used together with an existing yellow, cyan or black ink which is selected to be excellent in light fastness and water fastness, can provide a recorded product with excellence in light fastness and water fastness.

EXAMPLE

[0040] The present invention will be described below in more details with reference to Example. "part" and "%" in the description are shown by weight unless otherwise specified.

Example 1

[0041]

(1) To 450 parts of N,N-dimethylformamide were 51.0 parts of the compound represented by Formula 3 ($R_1=H$, $R_2=CH_3$), 23.9 parts of sodium carbonate, 18.0 parts of cupric acetate monohydrate, and 114.0 parts of 5-acetylamino-2-sulfoaniline added one after another under stirring, followed by increasing the temperature. The solution was put at 130-135°C for 3hrs to react, cooled, stirred at 20°C for 30 min, filtered, washed with 300 parts of methanol, and dried to obtain 62.9 parts of the No.1 compound as a red crystal.

To 471 parts of water was 513 parts of 96% sulfuric acid added dropwise to prepare 50% sulfuric acid, into which 61.3 parts of the No.1 compound was added. The solution was heated under reflux (at 123°C) for 3hrs to react, stirred under cooling (at about 25°C) for 1hr, filtered, washed with 120 parts of water to obtain a red wet cake. The wet cake was added gradually under stirring into a mix solution of 2000 parts of water and 80 parts of 24%

aqueous sodium hydroxide. The solution was stirred at the ambient temperature for 1hr, filtered to remove a little insoluble matter. To the filtrate was 100 parts of sodium chloride added under stirring. The solution was stirred at the ambient temperature for 1hr, filtered, and dried to obtain the No.2 compound as a red crystal.

(2) To 100 parts of ice water was 0.25 parts of Lipal OH(a nonionic surfactant, by Lion KK)added to dissolve and 10.1 parts of cyanuric chloride then added, followed by stirring for 15 min. To the solution was 18.0 parts of 2,5-disulfoaniline monosodium salt(purity 85.5%)added at 8-10°C, followed by dropping 10% aqueous sodium carbonate at the same temperature to maintain the pH to 2.7-3.0 for 4hrs for the first condensation reaction to obtain the solution containing the first condensate between cyanuric chloride and 2,5-disulfoaniline.

(3) To the reaction solution of (2) was 23.5 parts of the No.2 compound obtained in (1) added, followed by increasing the temperature and dropping 10% aqueous sodium carbonate at 60-65°C to maintain the pH to 4.3-4.7 for 1hr for the reaction. The solution was maintained for 30min at the pH 7-7.2, filtered to remove a little insoluble matter, and diluted with water to a liquid amount of 600 parts. To the solution was 72 parts of sodium chloride added under heating to maintain the temperature to 55-60°C, followed by stirring. After 1hr, the crystal was filtered to separate, washed with 75 parts of 10% aqueous sodium chloride, and dried to obtain 43.2 parts of the No.3 compound as a red crystal(sodium chloride content 33.7%, mirabilite content 0.1%).

(4) To a mix solution of 400 parts of water and 400 parts of methanol was 10.0 parts of the No.3 compound obtained in (3) added, followed by stirring under reflux for 1hr to dissolve and cooling on ice to deposit a clear red crystal. After stirring for 1hr, the crystal was filtered to separate, washed with 100 parts of methanol, and dried to obtain 6.4 parts of the desalted product of the No.3 compound(sodium chloride content 0.3%, mirabilite content 0.1% or less). λ_{max} :526nm(in water).

(5)The desalted product of the No.3 compound was conventionally used to prepare an ink, with which an image was printed out on the special paper (made by Canon KK)using an ink-jet printer. The test showed that the recorded image had a good water fastness and light fastness.

Example 2

[0042]

(1)9 parts of the No.3 Compound obtained in Example(3)was added in 180 parts of hot water having a temperature of about 80°C. To the solution was 10% aqueous sodium hydroxide added dropwise, followed by maintaining the pH to 11 at 85°C for 2hrs for the reaction. To the solution, after adjusting to a liquid amount of 250 parts, was 50 parts of sodium chloride added at 55-60°C, followed by maintaining the temperature to 55-60°C for 2 hrs. A deposited crystal was filtered to separate, and dried to obtain 7.6 parts of the No.4 compound as a red crystal.

(2) To 100 parts of water was 5.0 parts of the No.4 compound obtained in (1)added to dissolve and then 200 parts of methanol added, followed by stirring at 50-55°C for 1hr. A crystal was filtered and dried to obtain 3.3 parts of the desalted product of the No.4 compound as a red crystal. λ_{max} :526nm(in water).

(3) The desalted product of the No.3 compound was conventionally used to prepare an ink, with which an image was printed out on the special paper (made by Canon KK)using an ink-jet printer. The test showed that the recorded image had a good water fastness and light fastness.

Example 3

[0043]

(1) 11.7 parts of the No.2 compound obtained in Example(1)was added in 125 parts of pyridine and heated at 80°C. To the solution was 9.6 parts of p-toluenesulfonyl chloride added for 10 min, followed by maintaining the temperature to 100°C for 2hrs for the reaction and cooling on water. A crystal was filtered, washed with water and dried to obtain 12.2 parts of the No.27 compound as a red crystal.

(2) To 200 parts of water was 6.0 parts of the No.27 compound obtained in (1) added and then 2.4 parts of 24% aqueous sodium hydroxide added to adjust the pH to 11.5, followed by stirring for 1hr. To the solution, after adjusting to a liquid amount of 300 parts, was 22.5 parts of sodium chloride added, followed by stirring for 1hr and then filtering to obtain 16 parts of a wet cake. The wet cake was heated under reflux with 150 parts of methanol and 75 parts of water. After 1hr, the solution was filtered to remove a little insoluble matter, and stirred under cooling on ice for 1hr. The deposited crystal was filtered to separate, washed with a small amount of methanol and dried to obtain 4.0 parts of the desalted product of the No.27 compound as a red crystal.

Example 4

[0044]

- 5 (1) To 250 parts of N,N-dimethylformamide were 30.9 parts of the compound represented by Formula 3 (R_1 =ethoxycarbonyl group, R_2 =CH₃), 15.5 parts of potassium carbonate, 9.0 parts of cupric acetate monohydrate, and 53.0 parts of 5-acetylamino-2-sulfoaniline added one after another under stirring, followed by increasing the temperature to 110°C during 1hr. The solution was put at 110-120°C for 3hrs to react, cooled, poured into 2200 parts of water, stirred at 20°C for 1hr, filtered to remove a little insoluble matter. The filtrate was diluted with water to a liquid amount of about 3000 parts. To the solution was 450 parts of sodium chloride added under stirring, followed by stirring at the ambient temperature for 1hr. The deposited crystal was filtered to separate and dried to obtain 32.9 parts of the No.45 compound as a red crystal.
- 10 (2) To 145 parts of water was 156 parts of 96% sulfuric acid added dropwise under cooling to prepare 50% sulfuric acid, into which 32.7 parts of the No.45 compound was added. The solution was heated to increase the temperature to 75°C during 1 hr, and put at 75-80°C for 10 hrs to react. The reaction solution was cooled, poured into 400 parts of ice water, stirred at 20°C for 1hr, filtered and dried to obtain 25.4 parts of the No.46 compound.
- 15 (3) To 100 parts of pyridine was 10.4 parts of the No.46 compound added under stirring, followed by increasing the temperature to 90°C. To the solution was 6.9 parts of p-toluenesulfonyl chloride added during 30 min. The solution was put at 90-100°C for 3hrs to react, cooled, filtered to remove a little insoluble matter, poured into 350 parts of 10% sulfuric acid, and stirred at 20°C for 1hr. The deposited crystal was filtered, and dried to obtain 13.5 parts of the No.36 compound as a red crystal.
- 20

Example 5

25 [0045]

- (1) To 100 parts of ice water was 0.25 parts of Lipal OH added to dissolve and 10.1 parts of cyanuric chloride then added, followed by stirring for 15 min. To the solution was 14.0 parts of 5-sulfoanthranlyic acid (purity 88.4%) added at 8-10°C, followed by dropping 10% aqueous sodium hydroxide at the same temperature to maintain the pH to 2.7-3.0 for 3hrs for the first condensation reaction to obtain a reaction solution containing the first condensate between cyanuric chloride and 5-sulfoanthranlyic acid.
- 30 (2) To the reaction solution of the above (1) was 23.5 parts of the No.2 compound obtained in Example 1(1) added, followed by increasing the temperature and dropping 10% aqueous sodium hydroxide at 60-65°C to maintain the pH to 4.3-4.7 for 2hrs to react. The solution was filtered to remove a little insoluble matter to obtain a reaction solution containing the No.15 compound.
- 35 (3) To the reaction solution containing the No.15 compound obtained in the above (2) was water added to dilute the liquid amount to 600 parts, followed by dropping 10% aqueous sodium hydroxide to maintain the pH to 10.5 at 90°C for 2hrs to react. To the solution, after adjusting to a liquid amount of 800 parts, was a concentrated hydrochloric acid added dropwise at 55-60°C to adjust the pH to 2.7, followed by maintaining for 1hr. The deposited crystal was filtered to obtain a wet cake, which was heated together with 500 parts of methanol under stirring and maintained at 60°C for 1hr. The crystal was filtered to separate, washed with 100 parts of methanol and dried to obtain 36.0 parts of the desalted product of the No.16 compound as a red crystal. λ_{max} :520nm(as an ammonium salt in the aqueous solution).
- 40 (4) The desalted product of the No.16 compound was conventionally used to prepare an ink, with which an image was printed out on the special paper (made by Seiko-Epson KK)using an ink-jet printer. The test showed that the recorded image had a good water fastness and light fastness. Furthermore, it showed favorably no color change with alkali.
- 45

Example 6

50

[0046]

- (1) 10.0 parts of the No.3 compound obtained in Example 1(3)was added in 100 parts of hot water having a temperature of about 85°C. To the solution was 10.0 parts of 28% aqueous ammonia added, followed by heating at 80-90°C for 4hrs for the reaction(during which the pH decreased from 11.0 to 8.5). To the reaction solution was 10.0 parts of 28% aqueous ammonia added, followed by putting at 85 °C for 3hrs for the reaction(during which the pH decreased from 10.5 to 9.0). The reaction was confirmed to complete using HPLC(High Performance Liquid Chromatography). To the solution was 1.5 parts of Pearlite(trade name, diatom earth, made by Mitsui Kinzoku KK)
- 55

added, followed by stirring at 60-65°C for 15 min and filtering. To the filtrate was hot water added to adjust to a liquid amount of 200 parts, followed by heating to maintain the temperature to 60-65°C. To the solution were 30 parts of sodium chloride added at the same temperature and then a concentrated hydrochloric acid added to adjust the pH to 0.5 for crystallization. The solution, after stirring for 30 min, was filtered to give a wet cake of the No.5 compound. The wet cake was washed with 150 parts of methanol and dried to obtain the No.5 compound as a red crystal. λ_{max} :523nm(as an ammonium salt in the aqueous solution).

(2) The No.5 compound was conventionally used to prepare an ink, with which an image was printed out on the special paper (made by Seiko-Epson KK) using an ink-jet printer. The test showed that the recorded image had a good water fastness and light fastness.

Example 7

[0047]

(1) A solution containing the No.3 compound obtained in Example 1(3) was heated to 85°C. To the solution was 10% aqueous sodium hydroxide added dropwise under stirring to maintain the pH to 11 at 85°C for 2hrs for the reaction. To the solution was 8.0 parts of Pearlite added, followed by stirring for 10 min and filtering. To the filtrate were a concentrated hydrochloric acid added to adjust the pH to 6-7 and then 80 parts of sodium chloride added under heating to maintain the temperature to 60-65°C, followed by stirring for 30 min for salting-out. The crystal thus obtained was filtered to separate and washed with 40 parts of 20% aqueous sodium chloride. A wet cake thus obtained was heated together with 400 parts of water to 60-65°C. To the solution was a concentrated hydrochloric acid added dropwise under heating to maintain the same temperature during 1.5hrs, followed by adjusting the pH to 0.8 for crystallization. After stirring for 30 min, the crystal was filtered to obtain a wet cake of the No.4 compound. The wet cake obtained in the above (1) was heated together with 300 parts of methanol, stirred at 60-65°C for 1hr, and filtered. The crystal was washed with 200 parts of methanol and dried to obtain 31.3 parts of the desalted product of the No.4 compound as a red crystal.

(2) The desalted product of the No.4 compound was conventionally used to prepare an ink, with which an image was printed out on the special paper (made by Canon KK) using an ink-jet printer. The test showed that the recorded image had a good water fastness and light fastness.

Example 8

(1) Preparation of an ink

[0048] An ink for ink-jet printing of the present invention was produced by preparing the ink composition which contains the desalted product of the No.4 anthrapyridone compound obtained in Example 2 and has a composition as described in Table 2 below, and filtering it through a 0.45 μ m membrane filter.

Table 2

Ink composition	
Dyestuff(No.4)	7 parts
Water	73 parts
Glycerin	5 parts
Urea	5 parts
N-methyl-2-pyrrolidone	5 parts
Ethylene glycol	5 parts
Total	100 parts

[0049] An ink-jetting ink for reference was produced in the same procedure as described above except that C.I.Acid Red was used in place of the No.4 anthrapyridone compound.

(2) Ink-jet printing

[0050] By using an inkjet-printer (Trade name: BJF-600, made by Canon KK), ink-jet recording was done on an available glossy paper(Color BJ photo sheet film CA-101, made by Canon KK).

(3) Hue and vividness of recorded image

[0051] A recorded paper was subject to color determination using the colorimeter (GREATAG SPM50, made by GREATAG Co.) to calculate L^* , a^* , b^* values. Hue was evaluated by comparison with color samples of standard magenta in the "Japan Color Standard Paper" published by Japan Printing Machinery Manufacturers Association (JNC), and vividness C^* was evaluated by the formula:

$$C^* = ((a^*)^2 + (b^*)^2)^{1/2}$$

The results are shown in Table 3.

(4) Light fastness test of recorded image

[0052] A carbon arc fade meter (by Suga Testing Machine Co.) was used to irradiate carbon arc on the recorded papers for 20 hours. Grade was determined according to JIS blue scale.

(5) Water fastness test of recorded image

[0053] A recorded paper was set for 60min in a container whose space was saturated with water vapor at 100°C, and evaluated with respect to the influence by water(vapor) (ink bleeding from a printed region to non-printed regions). Evaluations were indicated by the following marks.

- : no bleeding observed
 Δ: a moderate bleeding observed
 X: a very big bleeding observed

The results in(1)-(5) are listed in Table 3.

Table 3

	Hue			Vividness	Light fastness	Water fastness
	L^*	a^*	b^*	C^*	Judgment (Grade)	Judgment
JNC Standard Magenta	46.3	74.4	-4.8	74.5	-	-
No.4 of. Example 2	48.4	81.0	-3.9	81.1	Grade 4	○
Ink for Reference	48.3	78.2	24.0	81.8	Grade 4	X

[0054] Table 3 reveals that the ink composition of the present invention shows the values in color close to those of JNC standard magenta and suitable for an ink-jetting magenta ink, and that it can give a recorded image which has an excellent water fastness in a highly humid atmosphere.

Example 9

[0055] The following tests were conducted using the ink compositions as described below.

(1) Ink compositions

Magenta ink

5 [0056]

M1: the ink composition of the No.4 compound obtained in Example 2

M2: the ink composition for reference

10 Cyan ink

[0057]

C1: the cyan ink composition containing C.I.Direct Blue 199(copper phthalocyanine type dyestuff)

15

(2) Ink-jet printing

[0058] The printings were conducted with the magenta ink only or with the magenta ink and the cyan ink overlapped using an ink-jet printer on the glossy paper(Color BJ photo sheet film CA-101, by Canon KK) supplied with a dyestuff-
20 acceptable layer to obtain the ink-jet printed matter.

(3) Light fastness of recorded (printed) image

[0059] The recording paper printed in the above (2) was subject to a 40hrs light fastness test using the acceleration
25 type xenon light fastness tester made by WACOM. The overlappingly printed image showed an excellent light fastness.

(4)Determination of color

[0060] Hues of the recorded image before and after the light exposure were measured to calculate the color differ-
30 ence(ΔE) using the above colorimeter. The results are shown in Table 4.

Table 4

35

	Printing	Glossy paper(ΔE)
1	M1 only	16.5
2	C1 overlapped on M1	15.4
3	M2 only	10.3
4	C1 overlapped on M2	24.5

40

[0061] In comparison of 2(the present invention) with 4(reference sample), both of which are blue colors obtained by double-printing (overlapping) cyan on magenta, 2 is apparently excellent because of a small ΔE . A combination of
45 the cyan ink containing a water-soluble copper phthalocyanine with the conventional magenta ink gave a large color change to bring about troubles to use. The magenta ink of the present invention, even if combined with the cyan ink, can give a good balance and a small color change. It can give an excellent overlappingly printed image in light fastness.

Example 10

50

[0062] A yellow ink(Y), a magenta ink(M), and a cyan ink(C)were prepared according to the same procedure as in Example 8. Printings were conducted by overlapping them to obtain the recorded images, which were evaluated and compared in value with the respective standard colors in the above JNC "Japan Color Standard Paper". The results were listed in Table 5, and the chromaticity diagram were shown in Fig.1.

55 Dyestuffs used in the respective inks were as follows:

Y: C.I.Direct Yellow 86

M: the dyestuff of the No.4 compound obtained in Example 2

C: C.I.Direct Blue 199

Table 5

	JNC Standard Dyestuff		Dyestuff of the present invention for ink	
	a*	b*	a*	b*
Yellow	-6.6	91.1	12.9	107.8
Red	68.5	48.1	68.2	59.3
Magenta	74.4	-4.8	81.0	-3.9
Blue	20.0	-51.0	26.9	-53.5
Cyan	-37.5	-50.4	-41.3	-48.3

[0063] Table 5 reveals that the ink of the present invention, if used in combination with a magenta ink, a yellow ink or a cyan ink, can give the hue and the blend hue close to those of the JNC standard. The magenta dyestuff of the present invention is industrially highly useful.

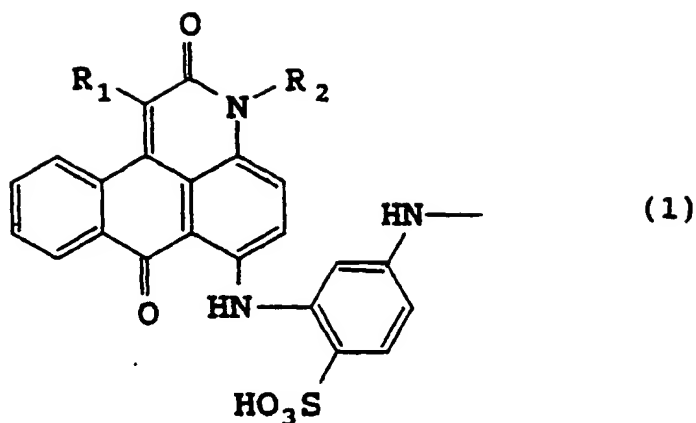
INDUSTRIAL APPLICABILITY

[0064] The anthrapyridone compound of the present invention is excellent in water-solubility, stable in storage and characterized by having a good ability to filter through a membrane filter in the production process of an ink composition. The dyestuff of the compound is highly safe for a humane body. Furthermore, the ink composition of the present invention using the anthrapyridone compound does not show a crystal deposition after a long storage, a change in property and a color change even in a summer season, so that it has good storage stability. The ink composition of the present invention, when used as a magenta ink for ink-jet recording, can provide a printed matter with excellence in light fastness and water fastness. Furthermore, the composition also, when used together with a yellow, cyan or black dye, can give an ink-jet recorded matter that is excellent in light fastness and water fastness. The composition also, even when used together with a metal phthalocyanine type dyestuff as a cyan, can keep a light fastness and, additionally, provide a clear printed surface as well as an ideal magenta color. The composition, when used together with a yellow or cyan ink, can provide a wide visible ray range of color tone.

[0065] Therefore, the ink composition of the present invention is very useful as a magenta ink for ink-jet recording.

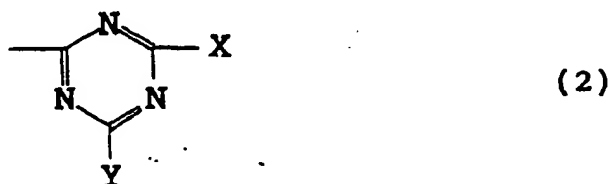
Claims

1. An anthrapyridone compound represented by Formula A-B or the salt thereof, wherein A is the dyestuff residue represented by Formula (1)



20 (In the formula, R_1 is hydrogen atom, an alkoxycarbonyl group or a benzoyl group and R_2 is hydrogen atom or methyl group); and B is hydrogen atom or a substituent group on the dyestuff residue A.

- 25 2. An anthrapyridone compound or the salt thereof according to claim (1), wherein said B is an acyl group or a group represented by Formula (2)



35 (In the formula, each X and Y is independently chlorine atom, hydroxyl group, amino group, monoethanolamino group, diethanolamino group, morpholino group or anilino group (which may have one or more substituents selected from the group consisting of sulfonate group, carboxyl group, methyl group and chlorine atom)).

- 40 3. An anthrapyridone compound or the salt thereof according to claim (2), wherein said X is anilino group (which may have one or more substituents selected from the group consisting of sulfonate group and carboxyl group), and Y is chlorine atom, hydroxyl group, amino group, monoethanolamino group, diethanolamino group or morpholino group.
- 45 4. An anthrapyridone compound or the salt thereof according to claim (2), wherein said acyl group is benzene sulfonyl group, tosyl group, 2-carboxy-benzoyl group or 3,4-dicarboxy-benzoyl group.
5. An anthrapyridone compound or the salt thereof according to claim (1), wherein said R_1 is hydrogen atom; R_2 is methyl group.
- 50 6. A water-based magenta ink composition which comprises containing the anthrapyridone compound or the salt thereof according to any one of claim (1) to (5).
7. A water-based magenta ink composition according to claim (6), wherein said composition contains water and an organic solvent.
- 55 8. A water-based magenta ink composition according to claim (6) or (7), wherein the content of inorganic salt included in said anthrapyridone compound or the salt is 1% by weight or less.

9. A water-based magenta ink composition according to any one of claim (6) to (8), wherein said composition is one for ink-jet recording.
- 5 10. A method for ink-jet recording which comprises using the water-based magenta ink composition according to any one of claim (6) or (8) as an ink, in the recording method that ink droplets are ejected responding to record signals to record onto a recording material.
- 10 11. A method for ink-jet recording which comprises using both the water-based magenta ink composition according to any one of claim (6) or (8) as an magenta ink and a water-based ink containing water-soluble metal phthalocyanine dyestuff as a cyan ink, in the recording method that ink droplets are ejected responding to record signals to record onto a recording material.
- 15 12. A method for ink-jet recording according to claim (11), wherein said recording material is an information transmission sheet.
13. A method for ink-jet recording according to claim (12), wherein said information transmission sheet is a surface-treated sheet.
- 20 14. An ink-jet printer which comprises being equipped with both a container receiving the water-based magenta ink composition according to any one of claim (6) or (8) and a container receiving the water-based cyan ink composition containing water-soluble metal phthalocyanine dyestuff.
- 25 15. An anthrapyridone compound or the salt thereof according to claim (1), wherein R_1 is hydrogen atom or a lower alkoxy carbonyl group; R_2 is methyl group; and B is hydrogen atom or a C1-C4 alkoxy carbonyl group.

30

35

40

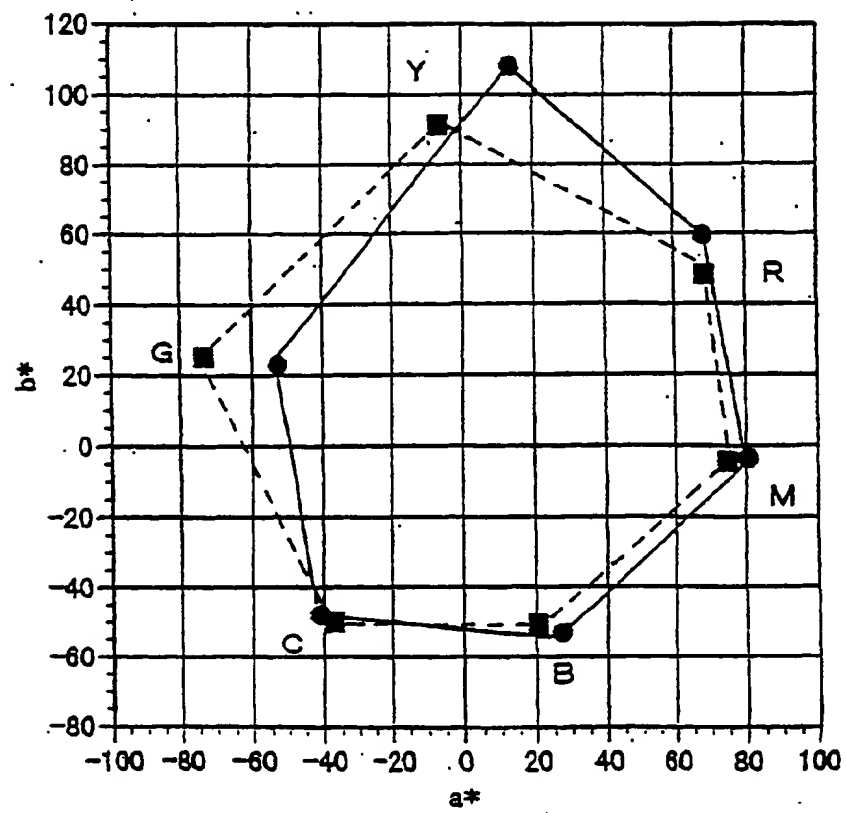
45

50

55

Fig.1

Chromaticity Diagram



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/01436

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ C09B5/14, C09D11/00, B41M5/00, B41J2/01 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ C09B5/14, C09D11/00, B41M5/00, B41J2/01 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAPLUS (STN), CAOLD (STN), REGISTRY (STN), WPIDS (STN)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X; Y	US, 2962497, A (Sandoz Ltd.), 29 November, 1960 (29. 11. 60), Claims 1 to 5 ; column 5, Table to column 7, Example 26 (Family: none)	1-5, 15; 6-14
Y	JP, 57-195775, A (Fuji Photo Film Co., Ltd.), 1 December, 1982 (01. 12. 82), Claims (Family: none)	6-14
A	US, 2759939, A (Sandoz A. G.), 21 August, 1956 (21. 08. 56), Claim 1 (Family: none)	1-5, 15
A	JP, 2-127483, A (Mitsubishi Kasei Corp.), 16 May, 1990 (16. 05. 90), Claims (Family: none)	6-14
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 26 April, 1999 (26. 04. 99)		Date of mailing of the international search report 18 May, 1999 (18. 05. 99)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

THIS PAGE BLANK (USPTO)